

SIEMENS



PATENT
Attorney Docket No. 99P9028US01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Inventor:	G. Merrill, et al.)		
)	Group Art Unit:	1725
Serial No.:	10/648,922)		
)	Examiner:	J. Johnson
Filed:	August 27, 2003)		

Title: HIGH TEMPERATURE EROSION RESISTANT COATING AND MATERIAL
CONTAINING COMPACTED HOLLOW GEOMETRIC SHAPES

Commissioner For Patents
PO Box 1450
Alexandria, VA 22313-1450

Sir:

SUPPLEMENTAL DECLARATION OF GARY MERRILL
UNDER 37 CFR 1.132

1. I, Gary Merrill, a citizen of the Great Britain, hereby declare and state in this Supplemental Declaration as follows:

2. I have been continuously employed by Siemens Westinghouse Power Corporation and its predecessor, Westinghouse Electric Corporation, since 1995. I am currently a Senior Engineer in the Materials Department, and work in the field of high temperature ceramic materials.

3. Prior to my employment by Westinghouse Electric Corporation, I was employed by Rolls Royce as an engineer for approximately seven years, working in the field of high temperature materials.

4. I received a bachelors degree in Materials Science & Engineering in 1988 from Brunel University, Great Britain (equivalent to a US masters degree). My combined academic and commercial experience in the field of materials science totals approximately sixteen years.

5. I understand that the USPTO Examiner has rejected certain claims in the above-cited application on the basis that the invention of those claims is anticipated and/or obvious by the teaching of Kamo (US Pat. No. 5,820,976). I understand that the Examiner's position is that the volcanic ash bubbles disclosed in Kamo have a wall thickness in the range of 50-500 micrometers.

6. On information and belief, I disagree with the Examiner's position that the volcanic ash bubbles disclosed in Kamo (composition: 80% SiO₂, 20% Al₂O₃) have a wall thickness in the range of 50-500 micrometers. The volcanic ash bubbles have an overall particle size of 10-90 microns. See col. 3 line 37.

7. As indicated in the attached technical paper titled "Sol-Gel Derived Ceramic Bubbles" authored by Kyung H. Moh, and published in 1995 in Volume 372 of the Materials Research Society symposium proceedings entitled "Hollow an Solid Spheres and Microspheres: Science and Technology Associated With Their Fabrication and Application", hollow spheres made of refractory volcanic ash bubbles comprising SiO₂ and Al₂O₃ have a typical bubble diameter of 1-120 micrometers and a typical wall thickness of 1-3 percent of the bubble diameter (see Table 1). Thus, the Kamo bubble diameter of 10-90 micrometers would fairly have a wall thickness in the range of 0.1- 2.7 micrometers. This calculation is very consistent with my previous estimate that "the wall thickness is quite likely toward the low end of a 2-40 micron range" provided in my prior Declaration.

8. Current commercially available refractory volcanic ash bubbles comprising SiO₂ and Al₂O₃, such as Recyclospheres™ manufactured by Sphere Services, Inc (www.sphereservices.com) and Cenospheres™ manufactured by Ashtek Corporation (www.ashtek.com), provide additional evidence of bubble diameter of 1-300 micrometers and wall thickness of 1-10 percent of the bubble diameter. Thus, assuming arguendo that these current commercially available bubbles are prior art, they still only have a wall thickness in the range of 0.1-30 micrometers.

9. Moreover, Kamo further explains that "increasing particle size above the range shown [10-90 micrometers] will result in a coating that is too thick, not durable, and weakly bonded to the substrate." See col. 4 lines 30-32. Accordingly, it is my opinion that Kamo does not disclose or suggest volcanic ash wall thickness in the range of 50-500 micrometers.

10. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or of any patent issuing there from.

Dated: 9th August 2005

By: G. B. Merrill

Gary Merrill

**Hollow and Solid Spheres and Microspheres:
Science and Technology Associated
With Their Fabrication and Application**

Symposium held November 3–December 1, 1994, Boston, Massachusetts, U.S.A.

EDITORS:

David L. Wilcox, Sr.

University of Illinois-Urbana
Urbana, Illinois, U.S.A.

Morris Berg

University of Illinois-Urbana
Urbana, Illinois, U.S.A.

Thomas Bernat

Lawrence Livermore National Laboratory
Livermore, California, U.S.A.

David Kellerman

Material Solutions-Kellerman Associates
Littleton, Massachusetts, U.S.A.

Joe K. Cochran, Jr.

Georgia Institute of Technology
Atlanta, Georgia, U.S.A.



MATERIALS RESEARCH SOCIETY
Pittsburgh, Pennsylvania

SOL-GEL DERIVED CERAMIC BUBBLES

KYUNG H. MOH
3M Company, St. Paul, MN.

ABSTRACT

Sol-gel derived ceramic bubbles include shaped and fired, porous or impermeable nonvitreous ceramic microcapsules of metal oxide and non-oxide, are made by non-melt process involving the equilibrium boiling point method with controlled thermal gelation. Discrete, free-flowing, ceramic microbubbles consist of a non-oxide component and/or an oxide component having diameters in the range of 1 to 300 micrometers and each having a wall thickness of less than 10 percent of the diameter of the bubble. In this process, a sol precursor and a bloating agent, when added to a bubble promoting medium under proper conditions, provide green gelled microbubbles which after firing are strong, well formed, ceramic microbubbles. The microbubbles are non-vitreous, sol-gel derived, fine microstructured, uniform, hollow, smooth, and are essentially all oxide or non-oxide or combinations of both. The microbubbles can be used as fillers for metal, glass, ceramic, and polymer or filled with a selected solid, liquid or gas for purpose of storing, transporting, or facilitating the use of the same.

INTRODUCTION

Different types of hollow spherical particles or microspheres from various refractory and glass materials have been disclosed and used in the past.¹⁻³ However, the microspheres and the processes by which they are made have one or more disadvantages which have limited their application and commercialization. Some of the disadvantages are microsphere size, quality, purity, cost of production, and high temperature capability of hollow microspheres produced.

Hollow glass microspheres from low melting point or high sodium content glass can not be used as fillers in electronic ceramic substrates or circuit boards because they cause poor dimensional stability of the fired substrate and sodium reacts with the electrode film of the circuit. Thick walled and porous hollow microspheres are difficult to use in circuit boards because of increased modulus and poor hermetic sealing of final products.

A method for the production of vitreous amorphous hollow microspheres is available which comprises heat-melting the glass at temperatures in the range of 1050° to 1500° C and blowing the melt off in the presence of a blowing agent to form hollow microspheres.⁴⁻⁶ However, this conventional method is not suitable for production of non-vitreous ceramic hollow microspheres. Furthermore, in such a conventional melt process, the average size of the microspheres produced is usually larger than 40 μm , and it is difficult to obtain small microspheres having a narrow particle size distribution, and high purity metal oxide and non-oxide composition microspheres.

Ceramic hollow microspheres derived from sol-gels have been developed.⁷⁻⁸ These include small sized, thin walled, free-flowing, impermeable non-vitreous ceramic microcapsules of metal oxide and non-oxide. The microspheres are made by non-melt processes involving liquid-liquid extraction, or equilibrium boiling point method with controlled thermal gelation. The most current process solves the problem of earlier sol-gel methods which required large quantities of dehydrating liquids for ceramic bubble production. Recent developments have demonstrated that high quality ceramic hollow microspheres can be produced at high yields in a variety of compositions by a simple process which requires a much smaller volume of forming medium and the forming medium can be easily recycled. This process is based on two phenomena: formation

of sol bubble structures via the equilibrium boiling method, and controlled gelation of such structures by submersion in a suitable hot forming medium.

EXPERIMENTAL PROCEDURE

Aluminum Borosilicate Composition Bubbles

Aluminum borosilicate sol precursor (40 g) having the calculated composition $3 \text{ Al}_2\text{O}_3 \cdot 1 \text{ B}_2\text{O}_3 \cdot 2 \text{ SiO}_2$ (see U.S. Pat. No. 3,795,524) was diluted with water to make a 16.5% fired solids solution.⁹ 20 g acetone and 0.8 g methyl cellulose (METHOCELTM, Dow Chemical Co., Midland, Mich.) were added with stirring to 80 g of the diluted aluminum borosilicate sol. The mixture (13.1% fired solids) was covered, to prevent evaporation, with inert wax sheeting (PARAFILM MTM, American Can Co., Greenwich, Conn.) and stirred until the initial white floc which formed dissolved. This sol was broken up by atomization and was sprayed into hot (95° C) oleyl alcohol. An atomizer from a spray-dryer, (Buchi, Switzerland) was positioned 9.5 cm from the surface of the hot oleyl alcohol. The air and sol feeding pressure to the atomizer were 0.7 kg/cm² and 0.5 kg/cm² respectively. The droplets formed small bubbles and floated on the surface of the oleyl alcohol. The stirred mixture was maintained at 95° C for 15 minutes. The gelled bubbles were separated by filtration, placed on a quartz dish and fired from room temperature to 900° C in air at the rate of 100° C/hour and held at this temperature for 1 hour. The sample was then allowed to cool with the furnace.

Mullite Composition Bubbles

With rapid stirring, 78 g of ammonia stabilized colloidal silica (NALCOTTM 2326, Nalco Chemical Co., Oak Brook, IL) was diluted 5 fold with 389 g D.I. water and quickly acidified by the addition of about 0.5 ml of concentrated HNO₃. This acidified silica sol was slowly added to a rapidly agitated solution of 319 g of aluminum formoacetate (9.5% aluminum oxide). The resulting mixture was concentrated by evaporation in an evacuated rotating flask to about twenty percent fired solids. To this was added in turn 10 g of lactic acid, 18 g of dimethylformamide (DMF), 48 g of acetone, and 2.13 g of Methocel powder (15,000 cP), and the resulting mixture was stirred until the initial white floc which formed and methocel powder were dissolved. The gelled microspheres were prepared as described above using oleyl alcohol maintained at 92°-95° C. The gel bubbles were separated by filtration and washed with ethanol, placed on a quartz dish and fired from room temperature to 1200° C in air at the rate of 100° C/hour and held at this temperature for 1 hour and cooled to room temperature.

Non-oxide Composition Bubbles

Zirconyl acetate (100 g; Harshaw-Filtro, Cleveland, Ohio) was diluted with water to make a 15% fired solids solution. Polyvinylpyrrolidone (18 g, 5% solution; PVP-K30TM, General Aniline & Film Corp., New York, N.Y.), 16.5 g of acetone, and 1.5 g of methyl cellulose powder were added with stirring to 167 g of the diluted acetate sol. The mixture was covered with wax sheeting and stirred until the initial white floc which formed dissolved. This sol was broken up by atomization and was sprayed into hot (95° C) oleyl alcohol. The preparation of gelled microspheres was the same as above examples. The droplets formed small bubbles and floated on the surface of the oleyl alcohol. The stirred mixture was maintained at 95° C for 15 minutes. The gelled bubbles were separated by filtration, washed with ethanol and mixed with cellulose fibers (SOLKA-FLOCTTM SW40, James River corporation, Berlin, N.H.) at the weight ratio of 1/4 before refiltration and drying at 80° C for 2 hours. Those mixtures of gel bubbles (ZrO₂ composition) and Solka-Floc powders were placed in a graphite mold (closed system) and fired to 1420° C and 1480° C in N₂ and Ar atmospheres by a controlled schedule (room temperature up to 1200° C over

the period
hours) and
furnace.

RESULTS

It is be
bloating a
medium o
bloating a
vapors or
boiling pc

In the
less than
reasonab
(e.g. sol
and a po
the like)

Expe
experim
wall thic
of about
are unif
chipping
Void
microsp

the period of 2 hours then 1200° C up to 1420° C and 1480° C, respectively, over a period of 1.5 hours) and held at these temperatures for 2 hours. The samples were then allowed to cool with the furnace.

RESULTS AND DISCUSSION

It is believed that droplets or microdroplets of a mixture of the sol precursor with a liquid bloating agent such as acetone or ethanol, on addition to a temperature controlled bubble promoting medium of oleyl alcohol, bloat and become microbubbles. It is believed that the low boiling bloating agent, on contact with the hot bubble promoting medium, vaporizes, and the resultant vapors or gases cause bubble formation. This overall process is referred to as the equilibrium boiling point method. A diagram of this bubble making process is shown in Fig. 1.

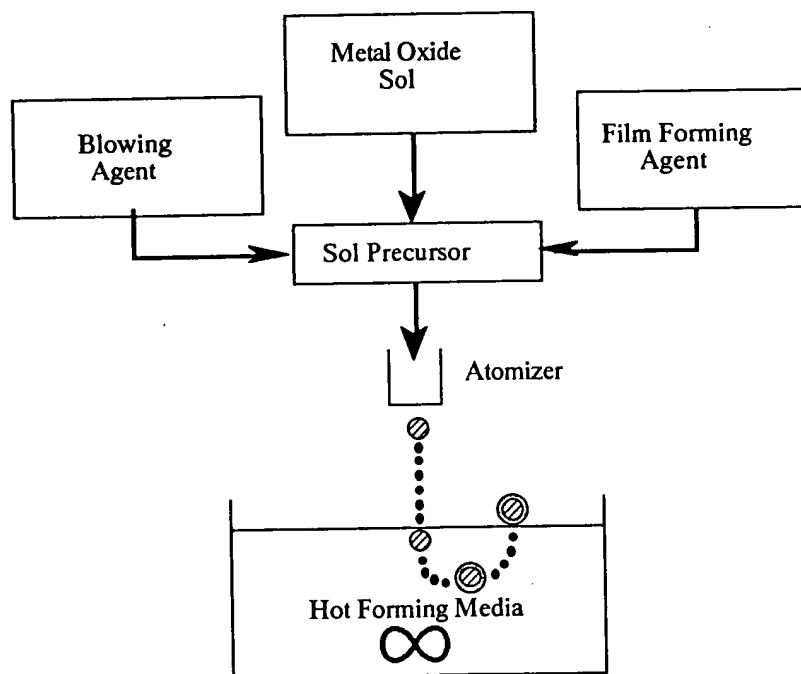


Fig. 1. Diagram of Bubble Making Process

In the gelation process, the bubble promoting medium is characterized by: low solubility (e.g. less than 1 weight percent) for the sol precursor and other sol ingredients including adjuvants: a reasonable degree of stability within the temperature range of use: inertness to chemical precursors (e.g. sol precursors, adjuvants, agglomeration preventative additive, etc.) of the resultant ceramic; and a possibility of recovering (by appropriate processing, e. g., to remove water, acetic acid and the like) and recycling the medium.

Experimental details and some physical characteristics for various microbubbles of this experiment are summarized in Table I. Hollow ceramic microbubbles in the oxide form having wall thicknesses of about 1 to about 8 percent of the diameter of the bubble and bubble diameters of about 1 to about 300 micrometers can be obtained. Microbubbles produced in this experiment are uniform in shape and wall thickness, transparent, tough, durable, highly resistant to scratching, chipping, and cracking.

Voids in the walls of the hollow microspheres of this experiment are avoided by firing the gelled microspheres at a temperature of 600° C or higher.

Table I. Experimental Details and Some Physical Characteristics for Various Microbubbles.

No	Composition	Starting materials	Film forming agent	Bloating agent	% Fired solids (w/o)	Bubble promoting medium	Firing temp (°C.)	Bubble size (μm)	W.T. ^e (%)
1	Alumina borosilica (3Al ₂ O ₃ . 1B ₂ O ₃ .2SiO ₂)	359 g ABS sol ^b precursor 111g D.I. water	180g 2% methyl cellulose powder solution	71.9% acetone	16.4%	oleyl alcohol (95° C.)	950	1-60	1
2	ZrO ₂	554 g zirconyl acetate 61.51 g colloidal zirconia. 76.01 g Y(NO ₃) ₃ .6H ₂ O	56.3 g 2% methyl cellulose powder solution	48.2g (43.4 cc) Freon 11/ methanol (50/50 vol.)	21.1%	oleyl alcohol (95° C.)	600	2-80	1-2
3	3Al ₂ O ₃ .2SiO ₂ with 2 w/o ^a B ₂ O ₃	1500 g sol. 465 D.I. water	750 g of 2% methyl cellulose powder solution	184 g (166cc) Freon 11/ methanol (50/50 vol.)	17.1%	oleyl alcohol (95° C.)	950	1-60	1-3
4	Mullite (3Al ₂ O ₃ . 2SiO ₂)	500 g concentrated mullite sol [mixture of A.F.A. ^c and Colloidal Silica (NALCO TM 2326)] 76.1 g DMF ^d	137 g 2% methyl cellulose powder solution	47.6g acetone	13.1%	oleyl alcohol (95° C.)	950	2-80	1
5	3Al ₂ O ₃ 1B ₂ O ₃ .2SiO ₂	83.0 ABS sol precursor 66.3 g D.I. water	0.8 g 2% methyl cellulose powder solution	10.2 g (9.2 cc) Freon 11/ methanol (50/50 vol.)	17.1%	mixture of oleyl alcohol and peanut oil (50/50 vol.)	950	40-120	2
6	ZrO ₂	2.2Kg zirconyl acetate. 270 g Y(NO ₃) ₃ .6H ₂ O	27 g methyl cellulose powder	291 g acetone	21.7%	oleyl alcohol (97° C.)	1.030	5-80	2-3

^a means weight percent fired oxides^b aluminum borosilicate sol precursor, see U.S. Pat. No. 3,795,524^c AFA (Aluminum formoacetate)^d DMF (Dimethylformamide)^e W.T. means wall thickness (% of bubble diameter)

This improves transparency, prevents both structural gaps or defects and any accompanying weakening effects and prevents absorption of moisture or other liquids that can degrade the microspheres. In general, higher firing temperatures promote densification of the walls of the ceramic microspheres. Depending on the particular oxide precursor material and firing temperature used, the walls of the fired ceramic bubbles will be porous and heat-sealable or impermeable. In general, the temperature required to seal the non-oxide bubbles will be higher than that required to seal the oxide bubbles. For example, TiO_2 bubbles can be sealed at temperatures in the range of 600° to 700° C. Titanium nitride can be sealed at about 1360° C.

Pressure within the sealed microbubbles will be dependent upon the temperature at which sealing is accomplished and the pressure of the select gas at that temperature. Thus, the pressure of the select gas and its pressure within the sealed microbubbles can be varied over a wide range, from sub-atmospheric (vacuum) to super-atmospheric, i.e., from 0.0001 to 2.0 or more atmospheres and approximated according to the gas laws. This process allows encapsulation of very pure gases and preselected combinations of gases.

The surface roughness is less than 2500 Angstrom units where surface roughness is defined as the average height of repeating or regular surface protuberances as measured vertically from the bottom to the apex of the protuberance using scanning electron microscopy (SEM).

Certain parameters can be considered and optimized to obtain well-formed hollow microbubbles. For example, concentration and hence, viscosity, of the mixture comprising the sol precursor, bloating agent, film forming agent, and other adjuvants, temperature range of the bubble promoting medium, and manner of addition of the mixture, in droplet form, to the bubble promoting medium can be varied to obtain ceramic bubbles of selected average diameter and wall thickness. Optimum values for these parameters can vary for different sol-gel precursors and their mixtures; that is, conditions to produce alumina-boria-silica microbubbles will not necessarily be the same as those for alumina-magnesia microbubbles. By choice of the proper conditions for these parameters, one can provide well-formed, spherical microbubbles having a single central cavity with walls of relatively uniform thickness.

Viscosity of the sol precursor mixture is in the range of 50-1000 cP. This viscosity range will limit the solid concentration range which can be used for a particular sol mixture. In general, raising the solids concentration is accompanied by an increase in viscosity. Use of higher solids concentrations or higher viscosity sols results in thicker walls and smaller diameters for bubbles generated from a particular precursor droplet size.

Concentration of the bloating agent can also be varied so as to change the size and wall thickness of the bubbles generated for a particular precursor droplet size. For constant sol concentration and droplet size, increasing the bloating agent concentration increases the average diameter and decreases the average wall thickness of the resulting bubbles. The ratio in parts by volume of sol precursor to bloating agent can be in the range of (70-99):(1-30).

Temperature of the bubble promoting medium affects the size, wall thickness and quality of the bubbles. Up to a certain limit, raising the temperature of the bubble promoting medium results in larger, thinner walled bubbles. This temperature limit depends on the concentration of the sol, the nature of the sol and the concentration of the bloating agent. Exceeding this temperature limit results in an increase in the percentage of broken bubbles in the final product. Raising the concentration of the bloating agent lowers this temperature limit. In general, raising the sol concentration raises this temperature limit. Further addition of various polymeric additives or film forming agents to the sol precursor can also raise this temperature limit. Temperature of the bubble promoting medium is maintained at 50° to 150° C.

To improve the physical and mechanical properties of the ceramic microbubbles produced by this method, defects or flaws in the form of broken bubbles and holes should be prevented.

Imperfections in the form of holes can be minimized by gelling the bubbles before the bubbles are allowed to contact each other. Bubbles can be broken by exposing the bubbles to an excessively high temperature of the bubble promoting medium and/or by incorporating an excess of the bloating agent.

Annealing and heat treatment steps in the hot bubble promoting medium assist in yielding intact, denser, and stronger gel bubbles by allowing the nascent, individual gel bubbles to gel completely as separate particles in the hot bubble promoting medium before contacting other particles during separation. The gelled bubbles need to be annealed at lower temperature (e.g., about 60°-80° C.)

after the bubble generation. After the annealing step, the bubbles are hardened by exposure to higher temperatures, e.g., 80° C. up to 115° C., before separating the bubbles from the bubble promoting medium.

Wall thickness of the bubbles can be controlled by a combination of suitable bloating agent, concentration, and viscosity of the sol precursor mixture: these parameters having been discussed above. Wall thickness can be measured by scanning electron microscopy (SEM) or transmission electron microscopy (TEM). Scanning electron micrograph of ceramic bubbles produced by this method are shown in Fig. 2.

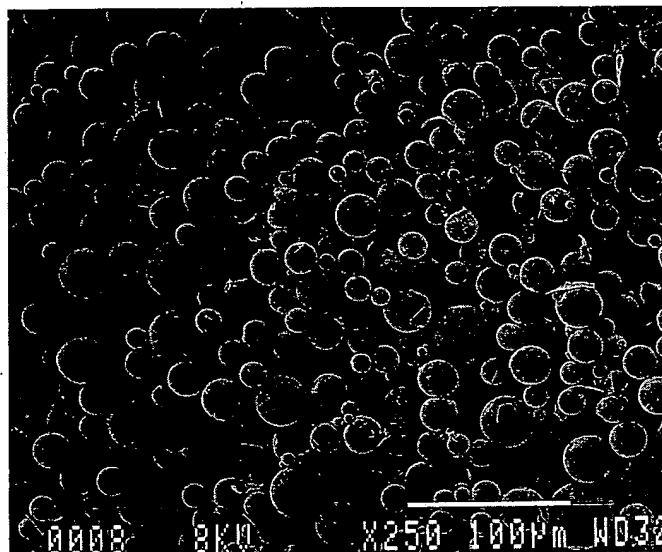


Fig. 2. Scanning Electron Micrograph of Ceramic Bubbles Produced by Sol-Gel Method.

Depending upon the particular sol precursor and firing temperature used, walls of the fired ceramic bubbles can be porous and heat sealable or dense and impermeable. The metal oxide in the bubble walls is present in whole or in part in the polycrystalline state or in an amorphous state capable of conversion, upon further firing, to the polycrystalline state. High temperatures seal the bubble walls. For example, dried, gelled microbubbles made from alumina-boria silica (ABS), can be fired to 1000° C, to provide a polycrystalline phase of aluminum borosilicate and an amorphous phase.

In general, higher firing temperatures in the range of 1000° C. to 1400° C. help to achieve hollow microbubbles with fully dense walls. In the firing process, these bubbles are loosely packed with a source of carbon to obtain a uniform, free flowing fired product. Some physical and mechanical properties of $3\text{Al}_2\text{O}_3 \cdot 1\text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$ composition ceramic microbubbles are recorded in Table II. In Table II, density was determined on those microbubbles that floated on ethanol, all contained in a separatory funnel. Contents of the separatory funnel were vigorously agitated (shaken) and allowed to settle. Density was determined on the floating microbubbles and the percent yield was determined to be the weight of the floating fraction divided by the total weight of the sample. Broken microbubbles and those with holes sank in ethanol during the agitation process. Packing factor was determined by dividing the bulk density by the true density. True density was determined following ASTM procedure D2840-69 "Standard Test Method for Average True Particle Density of Hollow Microspheres". Crush strength, reported in kilograms per square cm and parenthetically in pounds per square inch was measured according to ASTM procedure D3102-78 "Standard Practice for Determination of Isostatic Collapse Strength of Hollow Glass Microspheres" using glycerol in place of water. Sample number A is unfired bubble sample,

16.5% solids, sample number B is also unfired sample, 20% solids, and sample number C is the bubble sample fired at 950° C.

Table II. Physical and Mechanical Properties of $3\text{Al}_2\text{O}_3 \cdot 1\text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$ composition ceramic microbubbles.

Sample No.	Density (g/cc)		Float-ers	Packing factor	Crush strength collapse	
	Air pycnometer	Bulk			10%	20%
A	0.32	0.12	0.53	39	197 (2800)	844 (12,000)
B	0.66	0.33	0.54	50	323 (4600)	1125 (16,000)
C	0.76	0.32	0.59	42	197 (2800)	253 (3600)

Sintering temperatures of these sol-gel derived ceramic bubbles are hundreds of degrees below the temperatures that are required to convert conventional ceramic powder processed products to crystalline and dense ceramics. For example, the carbothermal reduction of TiO_2 by carbon followed by nitriding with nitrogen and/or ammonia gas has been shown to require high temperatures,¹⁰ e.g. 1600° C. By following the procedure described, we have prepared fully converted, fine microstructured titanium nitride ceramic bubbles from titania microbubbles at a temperature below 1400° C.

In the process of this experiment, a reducing agent, e.g., a source of carbon such as wood cellulose is mixed with the green bubbles prior to the firing step. The firing step can be carried out, for example, in an argon or a nitrogen atmosphere or in a mixture of the two gases.

When unfired or green titanium oxide containing microbubbles were fired in a bed of wood cellulose powder in a nitrogen atmosphere, an electrically conductive, fine microstructured (as determined by SEM) ceramic microbubbles of titanium nitrides were obtained. X-ray diffraction results showed that a mixture of nitrides and oxides was produced below 1420° C. in a nitrogen atmosphere, and above that temperature, the only crystalline phase detected was titanium nitride. X-ray diffraction (XRD) results for the samples of zirconium oxide containing microbubbles show that a mixture of ZrC and ZrO_2 is produced below 1480° C. in an argon atmosphere. Above that temperature, the only crystalline phase detected was zirconium carbide.

Non-oxide microbubbles of this experiment have the following general characteristics: diameter of about 1-300 micrometers: electrical resistivities of about 0.02-0.2 ohm.cm (as measured by a Simpson Ampere meter, Simpson Electric Co., Chicago Ill.), and are colored, depending on the composition. The walls can be fully dense with smaller than 0.1 micrometer grains or crystallites. For example, titanium carbide is black and non-transparent and both titanium nitride and zirconium nitride are gold colored.

It is believed that during firing of the green or oxide containing ceramic microbubbles in the presence of both a reducing atmosphere and a source of carbon such as wood cellulose, the wood cellulose is reduced to carbon or a carbon-containing intermediate phase, which causes conversion of the green or oxide containing ceramic microbubbles to non-oxide containing ceramic microbubbles.

Scanning electron microscope (SEM) micrographs showed that the sizes of individual crystallites present in the bubble wall of these microbubbles were smaller than 0.1 micrometers and

X-ray diffraction (XRD) studies revealed that the only crystalline phase found in the bubbles was nitride (e.g., TiN, formed at a firing temperature of 1360° C., and ZrN. 1420° C.) or carbide (TiC. 1420° C., ZrC. 1480° C.).

Some firing conditions and crystalline characteristics of some bubbles of this experiment are given in Table III.

Table III. Firing Conditions and Crystallite Characteristics of Some bubbles Fired in Different Atmospheres.

Starting Materials	Firing Conditions	Crystallite Phases	Crystallite Size (μm)	Resistivities (Ω · cm)
zirconyl acetate gel bubbles (φ: 20-100 μm, thickness: 0.2-1 μm)	with cellulose fiber powder	1360° C., 2 hrs	Ar atmos	ZrC ¹⁰⁰ , ZrO ₂ (T) ⁶⁰ , ZrO ₂ (M) ¹⁹
			N ₂ atmos	ZrN ¹⁰⁰ , ZrO ₂ (T/C) ³
	without cellulose fiber powder	1420° C., 2 hrs	Ar atmos	ZrC ¹⁰⁰ , ZrO ₂ (T) ⁸ , ZrO ₂ (M) ³
			N ₂ atmos	ZrN
		1480° C., 1 hrs	Ar atmos	ZrC
		1480° C., 2 hrs	N ₂ atmos	ZrN
		1480° C., 2 hrs	Ar atmos	ZrC ¹⁰⁰ , ZrO ₂ (M) ⁷⁴
			N ₂ atmos	ZrO ₂ (C) ¹⁰⁰ , ZrN ⁷⁴ , ZrO ₂ (M) ⁴¹
TiO ₂ gel bubbles (φ: 20-100 μm, thickness: 0.2-1 μm)	with cellulose fiber powder	1360° C., 2 hrs	Ar atmos	TiC ¹⁰⁰ , Ti ₂ O ₃ ²²
			N ₂ atmos	TiN
	without cellulose fiber powder	1420° C., 2 hrs	Ar atmos	TiC
			N ₂ atmos	TiN
		1480° C., 2 hrs	Ar atmos	TiC
			N ₂ atmos	TiN
TiO ₂ .Al ₂ O ₃ gel bubbles (φ: 20-100 μm, thickness: 0.02-1 μm)	without cellulose fiber powder	1480° C., 30 min.	N ₂ atmos	α-Al ₂ O ₃ ¹⁰⁰ , TiN ⁷⁶
	with cellulose fiber powder	1750° C., 1 hr	N ₂ atmos.	TiN ¹⁰⁰ , AlN ³⁵

φ: diameter.
ZrO₂(M): Monoclinic,
ZrO₂(T): Tetragonal,
ZrO₂(C): Cubic

SUMMARY

This work describes discrete, free-flowing, ceramic microbubbles consisting of a non-oxide component (or phase) and an oxide component (or phase). The microbubbles have diameters in the range of 1 to 300 micrometers (μm) and wall thicknesses of less than 10 percent of the diameter of the bubbles.

This work shows a sol-gel process which provides a high yield of high quality (uniform size and shape), thin-walled oxide containing and non-oxide containing ceramic microbubbles. A sol precursor and suitable liquid, referred to as a bloating agent, when added to a bubble promoting medium under the proper conditions, produce green gelled microbubbles which, after firing, are ceramic microbubbles having wall thicknesses less than 10 percent of the diameter of the bubbles. This process also produces microbubbles having encapsulated gases depending on the conditions under which the bubbles are formed.

This process uses a firing temperature range significantly below (about 300° C.) that range known to convert oxide containing ceramics to non-oxide containing ceramics.

The bubbles can be used to form shaped articles such as abrasives, catalyst supports, insulating materials, and electronic substrates.

REFERENCES

1. C.R. Schmitt, U.S. Patent No. 3,792,136 (12 Feb. 1974).
2. D.R. Watson, V.G. Carithers, and H.L. Drown, U.S. Patent No. 4,039,480 (2 Aug. 1977).
3. Y. Sarikaya and M. Akinc, *Ceramics International*, **14**, 239-244 (1988).
4. W.R. Beck and D.L. O'Brien, U.S. Patent No. 3,365,315 (23 Jan. 1968).
5. P.A. Howell, U.S. Patent No. 4,391,646 (5 Jul. 1983).
6. H.J. Marshall, U.S. Patent No. 4,767,726 (30 Aug. 1988).
7. H.G. Sowman, U.S. Patent No. 4,349,456 (14 Sept. 1982).
8. K.H. Moh, H.G. Sowman, and T.E. Wood, U.S. Patent No. 5,077,241 (31 Dec. 1991).
9. H.G. Sowman, U.S. Patent No. 3,795,524 (5 March 1974)
10. M. Yoshimura, M. Nishioka, and S. Somiya, *J. Mater. Sci. Lett.* **6**, 1463 (1987)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.